

UNITED STATES PATENT AND TRADEMARK OFFICE

I, John Neil Albert SWEENEY BSc, PhD, Dip. Trans. IoL,  
translator to RWS Group plc, of Europa House, Marsham Way, Gerrards Cross,  
Buckinghamshire, England declare:

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That I am well acquainted with the French and English languages.
3. That the attached is, to the best of my knowledge and belief, a true translation into the English language of the specification in French filed with the application for a patent in the U.S.A. on  
under the number
4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.

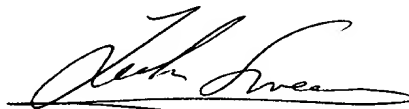


For and on behalf of RWS Group plc  
The 14th day of March 2001

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I, John Neil Albert SWEENEY BSc, PhD, Dip. Trans. IoL,  
translator to RWS Group plc, of Europa House, Marsham Way, Gerrards Cross,  
Buckinghamshire. England. hereby declare that I am conversant with the English and French  
languages and am a competent translator thereof. I declare further that to the best of my  
knowledge and belief the following is a true and correct translation of the accompanying  
documents in the French language.

Signed this 14th day of March 2001



J. N. A. SWEENEY

For and on behalf of RWS Group plc

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process makes it possible to achieve H<sub>2</sub>/CO ratios of 3 to 5, according to the steam throughput.

The second of these methods is mixed reforming. This is a process which operates under autothermal conditions, where the thermal energy necessary for the steam reforming over a catalyst is contributed by the partial combustion of the methane to CO<sub>2</sub>. The H<sub>2</sub>/CO ratio of the gases produced here is lower: typically between 1.5 and 2.5.

The third of these methods is the partial oxidation of the same hydrocarbons. This process does not require a catalyst. Combustion is carried out at 1 300-1 400°C without steam. This process is exothermic but produces less hydrogen than the preceding processes.

It should be noted that the steam reforming reactions mentioned above require catalysts, which are sensitive to the impurities present in hydrocarbons originating from oil or contained in natural gas. It is therefore necessary, prior to the reactions described, to carry out an exhaustive desulfurization of the hydrocarbons. In contrast, the partial oxidation also mentioned above makes it possible to use dirtier hydrocarbons but this process has the disadvantage of generating soot.

Once the H<sub>2</sub>/CO mixture has been produced according to one of the preceding methods, the reaction for the production of hydrogen by conversion of the CO in the presence of steam over a catalyst, according to the reaction:



can be promoted.

When it is desired above all to produce hydrogen, steam reforming seems to be the most advantageous process. In combination with the water gas reaction and with a process for the separation of the various gases produced, for example by Pressure Swing Adsorption (PSA), it makes it possible to obtain hydrogen of very good purity (comprising less than a

5 Merchant hydrogen currently originates  
essentially from the following processes:

10           (b)       the diversion of a portion of the  
hydrogen produced by captive producers when it is in  
excess;

15           (d)     the electrolysis of sodium chloride  
solutions, where hydrogen is coproduced at the same  
time as chlorine.

- by thermal cracking of ammonia,
- by catalytic reforming of methanol,
- by electrolytic dissociation of water.

The latter processes result in hydrogen with a high cost price because of the cost of the starting materials (in particular methanol) or of the energy consumption (5 kWh per m<sup>3</sup> of hydrogen produced for electrolysis). The thermal cracking of ammonia is a process which does not consume very much energy but the use of ammonia makes it a solution which is not very advantageous from the environmental viewpoint.

An advantageous alternative is to use catalytic generators of  $H_2/CO$  atmospheres for heat treatments (for example, for carrying out cementation treatments of metal components), to add a water gas reactor at the outlet to convert the  $CO$  to  $CO_2$  and hydrogen, and to separate the  $CO_2$ , the nitrogen possibly present and the hydrogen by methods known for this purpose.

5 a noble metal, such as platinum, nickel, rhodium or  
palladium. In these processes, it is necessary to add  
additional heating by burners or by an electrical  
element in order to achieve a temperature level  
sufficient for the reforming reactions, which are  
10 endothermic, to be able to be initiated. Part of this  
literature describes processes having the aim of  
improving and of controlling the temperature gradient  
in such reactors.

Thus, document GB-A-1 598 825 discloses an  
15 endothermic gas generator for the production of an  $H_2/CO$   
mixture intended for heat treatment. It preferably uses  
pure oxygen in order to avoid the external heat supply  
necessary for good progression of the reaction (which  
the presence of nitrogen would render necessary).

Document EP-A-450 872 shows a reactor in which an endothermic reaction, such as the production of an  $H_2/CO$  mixture by reforming of methane by water, is carried out. A burner is placed at the center of the reactor, which makes possible more efficient heating of the catalytic bed in which the reaction takes place.

The same principle is improved in document WO-A-90/03 218, by virtue of circulation of the combustion gases around the catalytic bed, which makes it possible to limit the radial and axial temperature gradients.

Document US-A-4 869 730 shows a U-shaped reactor in which an endothermic gas reaction takes place which makes possible the formation of a CO/H<sub>2</sub>/N<sub>2</sub> mixture. The reactor is heated externally by burners.

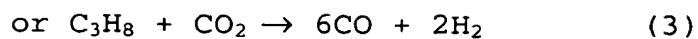
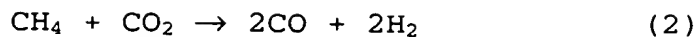
35 Provision has also been made to carry out the production of a hydrogen/CO mixture in an externally heated annular reactor. This reactor has a cylindrical general shape and comprises, in its central part, a cylinder sealed off at least at its lower end which can

either be empty or filled with an inert material or equipped with a heating means, such as an electrical element or a burner. The annular space of the reactor is filled with a catalytic medium. In comparison with a  
5 cylindrical reactor filled over its entire cross section with the catalytic medium, the annular reactor exhibits the advantage of decreasing the thermal gradients within the catalytic medium. The thickness of the catalytic medium is reduced and the transmission of  
10 the heat contributed by the external heating means is thus carried out more favorably therein. The optional presence of a burner or of other heating means in the central part of the annular reactor is also favorable from this viewpoint.

15 Each of the processes described above has disadvantages which make it difficult to apply them to small- or medium-sized plants for typically producing less than 1 000 m<sup>3</sup>/h of hydrogen. The capital cost required by steam reforming processes is crippling for  
20 small plants. The electrolysis of water is a process which is simple to operate and which is more suited to in situ production of hydrogen; on the other hand, it is a major consumer of energy. The thermal cracking of ammonia and the catalytic reforming of methanol are  
25 advantageous in terms of energy; on the other hand, the cost of methanol and the safety and environmental problems related to the use of ammonia make these processes difficult to operate industrially. As regards the presence of burners which heat the endothermic  
30 region of a catalytic reactor, it results in plants which are not very compact and which are poorly suited to units which have to produce small amounts of hydrogen. It is certainly possible to use elements to provide this reheating but this proves to be costly in  
35 terms of electric current.

Another way of proceeding consists in producing a hydrogen/CO mixture by carrying out the partial oxidation of a hydrocarbon (methane or propane, for example) by CO<sub>2</sub> according to the reactions:

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An advantageous way of carrying out this reaction consists in using a cylindrical reactor, in the upper part of which is inserted a radiant oxygen burner, also cylindrical, with a diameter substantially smaller than that of the reactor, fed with hydrocarbon and with oxygen. This oxygen burner descends as far as into the lower part of the reactor, where it introduces the combustion gases  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . This lower part of the reactor is filled with an inert packing (for example, based on alumina), in which emerge the said combustion gases originating from the oxygen burner, on the one hand, and in which arrive, on the other hand, the gases (hydrocarbon and  $\text{CO}_2$ ) necessary for reaction (2) or (3). It should be noted that the combustion reaction in the oxygen burner produces  $\text{CO}_2$  and steam, which are used in the reaction for the production of the hydrogen/CO mixture. All these gases are mixed inside the inert region and rise inside the reactor by passing through an annular region defined by the internal wall of the reactor and the external wall of the oxygen burner. It is in this annular region that reaction (2) or (3) takes place, as it is filled with a catalyst, which it is possible to maintain at a temperature of approximately  $1\ 200^\circ\text{C}$  as the result of its contact with the wall of the oxygen burner, despite the highly endothermic natures of reactions (2) and (3). The steam provided by the oxygen burner is sufficient by itself alone to prevent the formation of soot and the blocking of the reactor; no external steam supply is necessary for this purpose. The hydrogen/CO mixture produced is discharged from the upper part of the reactor and can be used on site or stored for use ex situ. The CO content of the mixture produced by the generator can advantageously be adjusted by introducing more or less  $\text{CO}_2$  into the lower part of the reactor in addition to the  $\text{CO}_2$  produced by the oxygen burner. A small reactor is thus obtained.



Nevertheless, a thermodynamic analysis shows that, if the heat recovery is correctly organized, it is possible to operate under autothermal conditions.

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35           - an excellent energy balance, making it  
possible to operate under autothermal conditions;

- excellent reliability and great simplicity;

- suitability for medium scale production, of the order of 100 to 1 000 m<sup>3</sup>/h.

5 To this end, a subject matter of the invention  
is a process for the production of a mixture comprising  
hydrogen and CO, of the type according to which partial  
oxidation of a hydrocarbon by an oxygenated medium or a  
medium capable of releasing oxygen is carried out, and  
10 according to which the processing is carried out under  
autothermal conditions, the heat given off by said  
oxidation being recovered to maintain the endothermic  
reactions which take place between the nonoxidized  
fraction of said hydrocarbon and the CO<sub>2</sub> and the steam  
15 produced by said oxidation, being characterized in  
that:

the reaction gas mixture comprising the hydrocarbon and the oxygenated medium is passed through a porous medium which has been preheated beforehand, thus making it possible to heat the reaction gas mixture by heat exchange with the porous medium to a temperature threshold sufficient to initiate combustion reactions, rendering unnecessary an external heat supply when operating continuously.

25           As will be clearly apparent to a person skilled  
in the art, the process according to the invention is  
based on combustion in a porous medium, during which  
the combustion gases return their heat to the porous  
medium to emerge from the reactor at a temperature  
30 close to the adiabatic temperature.

The filtration conditions, in particular the size of the beads generally constituting the porous medium and the flow rate of the gas, make it possible to adjust the temperature threshold. Thus, the combustion temperature is no longer solely a function of the calorific value of the fuel (adiabatic temperature) but is a function of the filtration conditions (flow rate, calorific value of the materials, size of the porous beads and porosity of the

medium, and the like). The result of this is that the combustion temperature can be greater than the adiabatic temperature.

Combustion in a porous medium has three main  
5 advantages.

First of all, it is possible to use fuel/oxidant mixtures outside the flammability limits. Thus, it is possible to burn mixtures with a very low charge of oxidant (the main application being the  
10 destruction of organic pollutants in air) or to burn very rich fuels and thus to use a low content of fuel.

Furthermore, the use of the energy is optimum (no losses). The temperature profile of the reactor exhibits a hot region, where combustion takes place, at an outlet temperature of the gases which is close to the adiabatic temperature. The reactor can operate under autothermal conditions, the only heat losses originate from heat exchanges with the wall of the reactor.

20           In fact, the combustion and the recovery of the heat are carried out in the same reactor. This leads to plants which are more compact than those employing a conventional combustion process and thus to a minimization of the heat losses.

25           The process according to the invention can  
furthermore adopt one or more of the following  
technical characteristics:

- said preheated porous medium is formed by a first inert porous material and the reaction gas mixture successively encounters said first inert porous material, a catalytic bed and then a second inert porous material.

- said first and second inert porous material are identical.

35           - said reaction gas mixture successively  
encounters said first inert porous material, said  
catalytic bed and said second inert porous material  
within a vertical cylindrical reactor, the ends of  
which are filled with one or other of said inert porous

materials and the central part of which is filled with said catalytic bed, the reactor being fed in alternate mode in the following way:

5 i) the reaction gas mixture is introduced in the lower part of the reactor and the mixture comprising the hydrogen and the CO is collected at the upper part of the reactor, or

10 ii) the reaction gas mixture is introduced in the upper part of the reactor (1) and the mixture comprising the hydrogen and the CO is collected at the lower part of the reactor,

passing from one of the introduction modes to the other ((i) (ii)) as a function of the advance of the combustion front inside the reactor.

15 - said reaction gas mixture successively encounters said first inert porous material, said catalytic bed and said second inert porous material within a reactor exhibiting the following arrangement:

20 a) a first cylinder comprising, at its lower end, means for introducing said reaction gas mixture;

25 b) a second cylinder of smaller diameter than said first cylinder, inserted into said first cylinder so that its upper end is situated at a distance from the upper end of the first cylinder and so that its lower end, via which the mixture comprising the hydrogen and the CO is collected, emerges outside the first cylinder;

30 c) said first inert porous material filling at least a portion of the height of the annular space defined by the internal wall of the first cylinder and the external wall of the second cylinder, said catalytic bed filling the upper part of the first cylinder and/or that of the second cylinder, and said  
35 second inert porous material filling the lower part of the second cylinder.

- the preheating of said porous medium is carried out using electrical elements situated at the periphery of the reactor.

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- the preheating of said porous medium is carried out by circulating therein, prior to said introduction of the reaction mixture, a preheating gas mixture comprising a hydrocarbon and oxygen which makes possible total combustion (for example in a ratio of 1 mol of methane per 2 mol of oxygen).

Examples of the implementation of the process according to the invention and of devices which make possible this implementation will now be described, with reference to the following appended figures:

- Figure 1, which shows a view in longitudinal cross section of a first example of a plant for the implementation of the process according to the invention;

- Figure 2, which shows a second example of a plant for the implementation of the process according to the invention.

The main component of the plant according to the invention represented in Figure 1 is a vertical cylindrical reactor 1 comprising a wall 2 and an internal space filled with a packing divided into several regions. In accordance with its vertical axis, the reactor 1 is divided into three directly superimposed regions each exhibiting a packing of predetermined nature. With respect to the embodiment represented, the lower part of the reactor 1 comprises a first packing 4 composed of an inert porous material (i.e. devoid of catalyst), such as alumina beads (in this instance with a mean diameter in the vicinity of 5 mm). The central part of the reactor 1 is itself packed with a catalytic bed 5 represented, for example, by a catalyst based on platinum deposited on an alumina support. The upper part of the reactor 1 comprises a second packing of inert porous material 6 identical to the porous material used for the lower part 4 of the reactor 1. The respective heights of these three packing regions 4, 5, 6 can vary according to the wishes of the operator but generally the packings 4 of the lower region 6 and of the upper region of the

reactor 1 are identical in height. In an implementational example which will be described later, each of the regions 4, 5, 6 represents substantially 1/3 of the working height of the reactor (that is to say, of the total height of the three packing regions 4, 5, 6).

At its lower and upper ends, the reactor 1 of the embodiment illustrated here comprises selective heating systems 7 and 7', for example electrical elements, the role of which in the preheating of regions 4 and 6 will be given in detail later.

The reactor 1 is fed with gas via a plant comprising:

a) an oxygen tank 8 (it will have been understood that this tank can also comprise any other oxygenated medium or medium capable of releasing oxygen, such as air, enriched air, CO<sub>2</sub>, and the like);

b) a tank 9 comprising a light hydrocarbon, such as methane, or a mixture of such light hydrocarbons.

An array of valves 10, 11, 12, of pumps 13, 14, 15 and of rotameters 16, 17, 18 makes it possible to regulate the throughputs and the proportions of these various gases, which are introduced into a common pipe 19 to form a CH<sub>4</sub>/O<sub>2</sub> gas mixture in proportions which vary according to requirements. This pipe 19 is subsequently subdivided into two branches 20, 21 which make it possible to introduce the gas mixture at the lower end of the reactor 1 or at the upper end of the reactor 1 respectively. The admission of the gases into one or other of these branches 20, 21 is controlled by two on-off valves 22, 23 situated respectively on the pipe 20 leading to the lower end of the reactor 10 and on the pipe 21 leading to the upper end of the reactor 1.

To make it possible to analyze the gases entering or departing from the reactor 1, pipes 24, 25 are attached to the pipes 20, 21 respectively and meet up to form a common pipe 26 leading to a plant for

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the diameter of the reactor 1 is favorable to an increase in the productivity of the plant.

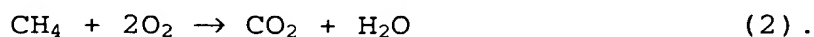
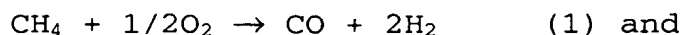
Two embodiments of the reactor 1 will now be described.

5           The first embodiment of the reactor of Figure 1 is not representative of the invention and is given only by way of comparative reference. The reactor 1 is filled solely with alumina beads with a mean diameter in the region of 2 mm and the gas is given a flow rate  
10 of approximately 0.5 m/s. When operating continuously, the respective proportions and the throughputs of the various gases injected or obtained are as follows:

- a total reaction mixture entering throughput of 2.3 m<sup>3</sup>/h (CH<sub>4</sub>-1/2O<sub>2</sub>),
- 15           - a content of hydrogen in the exiting mixture of 16.7% (when the theoretical maximum is 40%).

Preliminary calculations show that these conditions should theoretically make it possible to achieve temperatures of the order of 1 550°C. However,  
20 the results show that, whatever the operating conditions, the maximum temperature threshold achieved inside the reactor is of the order of 1 450°C. A degree of conversion of the methane of only 80% is then obtained. Furthermore, analysis of the outlet gases  
25 shows a significant divergence with respect to the theoretical concentrations calculated.

This limiting phenomenon can explained by the appearance of a heterogeneous catalysis process between the methane and the material of the porous medium  
30 (alumina). The combustion of the mixture then begins at a temperature which is too low to have a greater enhancing effect making it possible to achieve a critical threshold of 1 500°C. Furthermore, it is found that the temperature profile along the reactor has two  
35 regions. In the first region, exothermic reactions take place





5 which result in a rapid decrease in the temperature in the second region of the reactor. The high activation energy of reactions (3) and (4) results in a high dependence on the temperature of the overall operation of the reactor. Below 1 200°C, hydrogen  
10 production is virtually zero. Such an operating mode of the reactor 1 is thus clearly unsatisfactory.

In a first step, the on-off valves 23, 29 are closed and the on-off valves 22, 30 are open. In this way, the various gases composing the reaction medium are introduced via the lower part of the reactor 1 through the pipe 20 and the gases produced in the reactor 1 exit therefrom via its upper part to enter the pipe 25 (according to the continuous-line arrows in figure 1).

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necessary to take measures to limit the temperature in the catalytic medium 5, and temperatures of the order of 1 100°C can be introduced in the first inert porous packing 4. Under these conditions, a smaller volume of catalyst can be used. The thermocouples 32, 33, 34 make it possible to monitor the advance of the combustion front and thus to detect at what moment the latter approaches the catalytic bed 5. Typically, the combustion front advances at a rate of the order of 6 cm/min. Carrying out exothermic reaction (1) in the first inert porous packing 4 in this instance introduces a temperature of the catalytic bed 5 of between approximately 600 and 900°C under normal conditions, which makes it possible to maintain endothermic reactions (3) and (4) therein. The entire reactor then operates under autothermal conditions, according to the principles of combustion in a porous medium which were described previously.

When the data supplied by the thermocouples 32, 33, 34 to the data processing means 38 show that the combustion front has advanced in the direction of the upper part of the reactor 1, the data processing means 38 require the control means 39 to close the valves 22, 30 and to open the valves 23, 29. In this way, the reaction gases enter the pipe 21 and are now injected in the upper part of the reactor 1, so as to take advantage of the enthalpy of the second inert porous packing 6 situated at the upper part of the reactor 1 over which the preceding combustion front has just arrived. The gases produced in the reactor 1 exit therefrom via its lower part and enter the pipe 24 (according to the dotted arrows in figure 1). In the same way as above, this second inert packing 6 has been preheated beforehand by the electrical elements 7' or else is heated at the beginning of the reaction process by an enrichment of the gas mixture with oxygen. Likewise, the thermocouples 35, 36, 37 monitor the advance of the combustion front, thus making it

possible to detect at what moment the latter approaches the catalytic bed 5, and the like.

The reactor 1 can thus be operated in "alternate flow" in the way which has just been described, guaranteeing an operating mode which makes it possible to avoid a rapid deterioration in the properties of the catalytic bed 5.

Under the experimental conditions which have been described and for a total entering throughput in the region of 1 m<sup>3</sup>/h with a CH<sub>4</sub>/O<sub>2</sub> ratio equal to 2.1 (for an entering pressure in the region of 1 bar), an outlet mixture is obtained for which the CH<sub>4</sub>/H<sub>2</sub> ratio (yield) is in the region of 1.7 (the maximum theoretical yield being 2), the gas exiting from the plant comprising approximately 40% of hydrogen, 2% of CH<sub>4</sub> and 17% of CO.

Another device according to the invention, represented in figure 2, comprises two overlapping cylinders. The first cylinder 40 comprises, at its lower part, a pipe 41 via which the mixture of hydrocarbon and of oxygenated medium intended to produce the desired H<sub>2</sub>/CO/N<sub>2</sub> or H<sub>2</sub>CO mixture can be introduced. The second cylinder 42, with a smaller diameter than the preceding cylinder, is inserted so that its external surface defines an annular space with the internal surface of the cylinder of large diameter 40. The upper end of the second cylinder of small diameter 42 is situated at a distance from the upper end of the first cylinder of large diameter 40 and the lower end of the second cylinder of small diameter 42 emerges outside the first cylinder of large diameter 40. After their entry into the cylinder 40, the gases of the reaction mixture pass through a packing 43 forming an inert porous medium comparable to the inert porous packings 4, 6 of the plant of figure 1. This packing 43 can be, for example, composed of alumina beads with a mean diameter of approximately 5 mm. In the upper part of the first cylinder 40, this inert packing 43 is replaced by a catalytic bed 44

In the same way as in the reactor of figure 1, the combustion reaction between the methane and the oxygen begins inside the inert porous medium 43. The heat given off by this reaction is passed on to the catalytic bed 44 so as to compensate therein for the endothermic effect of reforming reactions 3, 4 which take place therein. Here again, it is possible to determine the various operating parameters of the reactor for the latter to operate under autothermal conditions, thus without any external heat supply being necessary, apart from possibly during the initiation phase of the combustion operation via the element 46 or via by a preheating phase which is superstoichiometric with respect to oxygen.

Under the experimental conditions which have been described and for a total entering throughput of

1.5 m<sup>3</sup>/h with a CH<sub>4</sub>/O<sub>2</sub> ratio equal to 1.9 (for an entering pressure in the region of 1.8 bar), an outlet mixture is obtained for which the CH<sub>4</sub>/H<sub>2</sub> ratio (yield) is in the region of 1.6 (the maximum theoretical yield being 2), the gas exiting from the plant comprising approximately 37.1% of hydrogen, 4.2% of CH<sub>4</sub> and 14.6% of CO.

As an alternative form, it can be envisaged for the inert porous packing 43 to fill the cylinder 40 of large diameter as far as its upper end. The catalytic bed 44 is then present only in the upper part of the cylinder of small diameter 42.

With such a reactor of the "countercurrentwise flow" type, an efficiency is obtained which is somewhat lower from the viewpoint of the heat recovery than with the preceding reactor, referred to as an "alternate flow" reactor. To achieve the same efficiency, an alternate flow reactor must comprise greater exchange surface areas than in the case of a countercurrentwise flow reactor. On the other hand, the countercurrentwise flow reactor operates in a stationary manner and does not require any control means targeted at regularly reversing the directions of the gas flows.

In both the reactor cases which have just been set out, it is apparent, with experience, that the cooling of the gases resulting from the reaction is sufficiently rapid to prevent decomposition of the CO, which would form soot. Such a formation of soot only occurs when the CH<sub>4</sub>/O<sub>2</sub> ratio is increased substantially beyond the stoichiometric ratio.

Operation under pressure is also possible. It should be noted that the reaction gases enter the reactor at ambient temperature, which eliminates any risk of flammability, in particular when the pressure is increased. Tests carried out at 10 bar, with operating conditions similar to those described in the example, on the reactor of "alternate flow" type have made it possible to generate H<sub>2</sub>/CO mixture comprising 35% of hydrogen.

These types of reactors are relatively simple in design and are reduced in size, and do not require an external energy supply, except for the transitory initiation period. This preheating can, as has been  
5 seen above, advantageously be carried out by total combustion of the hydrocarbon, which makes it possible to dispense with the addition of electrical elements while decreasing the start-up time. They thus exhibit an altogether lower operating and capital cost. This  
10 renders them highly advantageous with respect to the endothermic catalytic oxidation processes previously used for the production of  $H_2/CO$  mixtures.